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(54) Chromate-free protective coatings

(57) The invention provides chromate-free coating mixtures, and coatings formed from these mixtures, that protect an underlying aluminum or aluminum alloy substrate from corrosion. The coating mixtures include a continuous phase selected from organic polymeric compositions, or sol-gels, and a distributed phase, dispersed or dissolved throughout the continuous phase. The distributed phase includes the corrosion-inhibiting chromate-free salts. In accordance with the invention, the mixture of salts includes (1) a first salt selected from (a) the esters of rare earth metals, such as cerium and lanthanum oxalates and acetates, and (b) the vanadate salts of alkali and alkali earth metals, such as sodium metavanadate and calcium metavanadate; and (2) a

second salt that is a borate salt of alkali earth metals, such as barium metaborate. In certain embodiments, the coatings of the invention include both (a), and (b), in conjunction with the borate salt (2). In other embodiments, the chromate free salt is a chloride of a rare earth metal, or mixture of such chlorides, either alone or in combination with the first salt or the second salt, or both the first and second salts. Coatings of the invention provide protection to an underlying substrate, even after subjection to a 3000 hour salt spray test. Moreover, the coatings are resistant to degradation by SKYDROL, and are able to withstand impacts of 50 inch-pounds (forward) and 30 inch-pounds (reverse), so that they are well suited for use as protective coatings for aircraft.

a third monomer in the flow control copolymer of OH no. -0-100. The copolymer flow modifiers enhance the rheol. of the curable film-forming resinous material like thermosetting powder coating compns. to provide for smoother coatings while at the same time not adversely affecting appearance or adhesion with assoc. coatings, e.g., base coat/clear coat. A powder coating clear coat compn. contg. PD 9060 binder, dodecanedioic acid crosslinker, flow modifier N,N-dimethylaminoethyl methacrylate-2-ethylhexyl acrylate-2-hydroxyethyl acrylate copolymer (amine equiv. 0.093 mequiv, OH no. 21.7), benzoin, stabilizers, wax, cyclic organophosphorous, Me dicocoamine, and triphenyltin hydroxide was sprayed onto a ED 5051 panel and cured at 285°F for 30 min to give a coating having crater resistance (1 = poor, 3 = very good) rating 3, vs. 1 using Et acrylate-2-ethylhexyl acrylate copolymer flow modifier.

127: 221976r Thermoreversible polymeric thickener. Ohsumi, Tatsuya (Sanyo Chemical Industries, Ltd., Japan) U.S. 5,658,981 (Cl. 524-555; C08F26/00), 19 Aug 1997, US Appl. 196,112, 18 Nov 1994; 12 pp. Cont. of U.S. Ser. No. 196,112, abandoned. (Eng). A thermoreversible thickener comprising a water-sol. copolymer contg. as constituent monomer at least 50% by wt. of a vinyl carboxylic ester of an alkoxylated C₂₋₅ amine. The thickener, with a transition temp. which can be easily controlled according to the purpose of application such as coating, rolling oil, adhesives or inks, has a characteristic such that heating the aq. soln. thereof up to a temp. above the transition temp. causes rapid thickening of the soln. A typical thickener was manufd. by polymn. of 90 parts 2-morpholinoethyl methacrylate with 10 parts methacrylic acid and tested in waterborne coatings.

127: 221977s Manufacture of nonaqueous polymer dispersions as antisagging agents for coatings. Oka, Kenji (Nippon Oil and Fats Co., Ltd., Japan) Jpn. Kokai Tokkyo Koho JP 09,202,802 [97,202,802] (Cl. C08F2/08), 5 Aug 1997, Appl. 96/11,418, 26 Jan 1996; 9 pp. (Japan). The dispersions are prep'd. by soln. polymn. of vinyl monomers added dropwise in org. solvents which do not dissolve the vinyl polymers but dissolve dispersion stabilizers prep'd. by addn. reaction of linear polyesters with CO₂H at one end and glycidyl-contg. acrylic polymers; the org. solns. contain 0.001-0.5% (on monomers) radical polymn. initiators. Thus, 27.87 parts 6.74:28.79:46.72 2-ethylhexanoic acid-hexahydrophthalic anhydride-Cardura E 10 polycondensate and 70.79 parts 27.0:6.1:4.8 2-ethylhexyl methacrylate-2-hydroxyethyl methacrylate (I)-glycidyl methacrylate (II) copolymer reacted to form a stabilizer, 16.00 parts of which was dissolved in 22.00 parts mineral spirits with 0.05 part tert-Bu peroxy-2-ethylhexanoate (III). A mixt. comprising Me methacrylate 15.30, acrylic acid 2.40, I 11.20, acrylonitrile 1.60, II 2.20, III 0.27, and mineral spirits 27.86 parts was added dropwise to the dispersant soln. at 95-100° and heated at 120° for 2 h to give an acrylic polymer dispersion (av. particle size 141 nm) imparting good antisagging properties to an acrylic coating.

127: 221978t Aqueous conductive coating composition. Kondo, Yosuke (Shinto Paint Co Ltd, Japan) Brit. UK Pat. Appl. GB 2,307,913 (Cl. C09D5/24), 11 Jun 1997, JP Appl. 95/345,530, 7 Dec 1995; 12 pp. (Eng). A water-dilutable and conductive coating compn. whereby any desired color can be afforded, is characterized in that, said compn. contains 10-50% by wt. of water-sol. or water-dispersible synthetic resin (non-volatile content) and 5-40% by wt. of white electroconductive pigment such as Dentol WK-300 (Sn oxide-Sb oxide-coated K titanate) and the compn. is such that the amt. of each of sodium and potassium in the resulting coated film is not more than 330 ppm.

127: 221979u Improvement of dispersibility of post-treated titanium dioxide pigments. Luginsland, Hans-Hermann; Tiedemann, Peter; Elfenthal, Lothar; Blumel, Siegfried (Kronos Titan-GmbH, Germany) Ger. Offen. DE 19,607,249 (Cl. C09C1/36), 28 Aug 1997, Appl. 19,607,249, 27 Feb 1996; 6 pp. (Ger). Titania dispersibility is improved when the pigment particles are subjected to an air sorting process before surface treatment and final milling. The filterability of the final product is thereby facilitated.

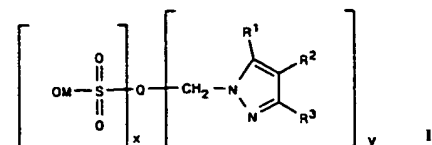
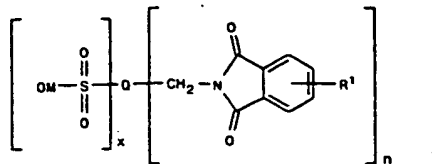
127: 221980n Manufacture of black pigment with good affinity to water, solvents, or organic polymers. Hirayama, Takayuki; Sato, Haruyoshi; Otsuki, Hiroshi (Nippon Oil Co., Ltd., Japan) Jpn. Kokai Tokkyo Koho JP 09,217,022 [97,217,022] (Cl. C09C3/10), 19 Aug 1997, JP Appl. 95/318,161, 6 Dec 1995; 16 pp. (Japan). The process giving a black pigment useful for light-shielding coat with low cond. comprises contacting a polymer having OH content 5-500 mmol/100g and optionally carboxylic content 30-300 mmol/100 g with a carbon material at 50-250°. Prep'd. a Bu cellosolve varnish (A) contg. iso-Bu acrylate, Bu acrylate, Me methacrylate, hydroxyethyl acrylate, and acrylic acid copolymer, kneading the varnish with C black (Special Black 4), and stirring with glass beads gave a paste. Dispersing the paste 100, varnish A 50, Sumimal M66B 25, and NEt₃ 8 parts in water as a 20% soln. gave an electrodeposited coating compn.

127: 221981p Blackened cuprous oxide composite powder for antifouling paints. Carlton, John N. (American Chemet Corp., USA) PCT Int. Appl. WO 97 31,054 (Cl. C08K3/00), 28 Aug 1997, US Appl. 604,736, 21 Feb 1996; 18 pp. (Eng). A composite cuprous oxide powder comprising ≥80% cuprous oxide particles and surface oxidized cupric oxide is produced by subjecting particles of cuprous oxide to surface oxidn. at -400-900°F. Oxidn. tests of Cu₂O at 500°, 700°, and 900° gave compns. of Cu₂O 96.9 and CuO 1.06, Cu₂O 93.21 and CuO 4.84, and Cu₂O 65.24 and CuO 32.91%, resp.

127: 221982q Dyeing of textile from colorant extracted from recycled wood. Sanbongi, Nobuko (Sanbongi, Nobuko, Japan) Jpn. Kokai Tokkyo Koho JP 09,228,260 [97,228,260] (Cl. D06P1/34), 2 Sep 1997, Appl. 96/70,852, 19 Feb 1996; 2 pp. (Japan). The process is

carried out by boiling of wood from recycled wood chips, filtration with a bleached cotton and dyeing of a kind of textile to give a finished textile with natural wood colors.

127: 221983r Pigment compositions containing quinacridone derivatives for coatings. Hendi, Shivakumar Basalingappa (Ciba Spezialitaetenchemie Holding Ag, Switz.) Eur. Pat. Appl. EP 790,281 (Cl. C09B67/22), 20 Aug 1997, US Appl. 11,566, 13 Feb 1996; 11 pp. (Eng). Pigment compns. comprise a pigment and both phthalimidomete-



hylquinacridone I and pyrazolylmethylquinacridone II as additives (Q = quinacridone radical; R' = H, halogen, C₁₋₄ alkyl; R¹⁻³ = H, halogen, unsubstituted C₁₋₈ alkyl, C₁₋₈ alkyl substituted by halogen or C₁₋₈ alkoxy, unsubstituted C₆₋₁₀ aryl, C₆₋₁₀ aryl which is substituted by C₁₋₈ alkyl, halogen, nitro, C₁₋₆ alkoxy group; or R¹, R² together with the carbons of the pyrazole ring form part of a fused alicyclic, arom. or heterocyclic ring; M = H, ammonium cation, metal cation; n = 1-4; x = 0-2; y = 1-4). The pigment compns. are useful for coloring coating compns. Coating compn. colored with the inventive pigment compns. have excellent rheol. characteristics and which yield coatings having excellent satn.

127: 221984s Chromate-free protective coatings for aircraft. Hager, Harold E.; Blohowiak, Kay Y.; Jones, John H.; Johnson, Chris J.; Wong, Chun M.; Taylor, Ray S.; Cook, Robert L., Jr. (Boeing Company; University of Virginia Patent Foundation, USA) Eur. Pat. Appl. EP 792,922 (Cl. C09D5/08), 3 Sep 1997, US Appl. 607,514, 27 Feb 1996; 13 pp. (Eng). The chromate-free coating mixts., and coatings formed from these mixts., protect an underlying aluminum or aluminum alloy substrate from corrosion in a 3000-h salt spray test. The mixts. include a continuous phase comprising org. polymeric compns. or sol-gels and a distributed phase, dispersed or dissolved throughout the continuous phase. The distributed phase includes (1) a first salt selected from (a) rare earth metal salts of org. acids, such as Ce and La oxalates and acetates, and (b) alkali and alk. earth metal vanadates, such as Na metavanadate and Ca metavanadate; and (2) a second salt which is an alk. earth metal borate, such as Ba metaborate. The chromate free salt may also be a rare earth metal chloride or mixt. of such chlorides, either alone or in combination with the first salt and/or the second salt.

127: 221985t UV-absorbing acrylic polymer compositions. Nishida, Hideo; Takishita, Katsuhisa; Arimoto, Kunio; Samukawa, Seiji; Watanabe, Kazuyuki; Ikkaku, Yasuhiko (Ishihara Yakuhin Co., Ltd.; Kyodo Chemical Co., Ltd.; Kaku Kogyo K. K., Japan) Jpn. Kokai Tokkyo Koho JP 09,202,874 [97,202,874] (Cl. C09K3/00), 5 Aug 1997, Appl. 96/32,960, 25 Jan 1996; 7 pp. (Japan). The compns., giving water-sol. coatings, contain copolymers prep'd. from (meth)acrylic acid esters 10-50, polymerizable UV-absorbing compds. 10-50, and unsatd. carboxylic acids 10-50%; and 0.1-1.3 equiv (based on the carboxy group of the copolymers) amino compds. and/or alkali metal hydroxides. Thus, a compn. contg. cyclohexyl methacrylate-2-[2-hydroxy-5-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]-5-chlorobenzotriazole-methacrylic acid copolymer 30, methyl diethanolamine 2, polyether-modified silicone 3, and isopropanol 65 parts was applied on glass to give coatings, which can be removed by water.

127: 221986u Binder compositions containing cyclic carbonate group-containing oligomers or polymers and amine group-containing crosslinking agents, coatings containing the binder, and substrates provided with the coatings. Stanssens, Dirk Armand Wim; Van Den Elshout, Wilhelmus Henricus Hubertus Antonius; Tijssen, Pascal Maria Hubert Pierre (DSM N.V., Neth.) Belg. BE 1,009,543 (Cl. C08G59/14), 6 May 1997, Appl. 95/688, 11 Aug 1995; 16 pp. (Neth). In the compns., the crosslinking agent has functionality ≥2 and contains primary amine groups bonded in in β-, γ-, or δ-position to a tertiary amine group. The crosslinking agent has general formula (NH₂R¹)_m(NR²)_n (R¹ = linear or branched C₂₋₄-hydrocarbon moiety; R² = alkyl, cycloalkyl, or arom. group of a heteroatom-contg. moiety, and may bond several tertiary N atoms together; m = 1, 2, or 3; n = 3 - m). The coatings contain a binder, fillers and/or pigments, and, optionally, the usual additives. The coating on the coated substrates is hardened. At 110° were added to methoxypropanol 400, Me methacrylate 420, methacryloyloxypropylene carbonate 120, 2-ethylhexyl acrylate 60, and tert-butylperoxy-2-ethylhexanoate 30, and then a soln. consisting of tert-butylperoxy-2-ethylhexanoate in methoxypropanol 30 g. A clear coat binder was obtained using a mixt. of the above polymer 10 with MEK 2.6 and 4-cascade:1,4-diaminobutane[4]:propylamine 0.43 g. Steel was coated with the material.

Description

Field of the Invention

5 The invention relates to coatings, and mixtures that form these coatings, that are chromate-free and that provide protection against corrosion of an underlying metallic substrate. More particularly, the chromate-free, corrosion-inhibiting coatings of the invention provide protection of aluminum and its alloys against corrosion, and are therefore useful in several applications, including the aircraft industry.

Background of the Invention

10 Aluminum and its alloys have found increasing use in recent years in many industrial and consumer applications due to their light weight and high strength properties. Aircraft airframes and outer skins are among the more demanding applications for aluminum and its alloys. In order to preserve the large capital investment in aircraft, it is necessary to protect the aircraft from corrosion that is frequently initiated by environmental factors, such as water, oxygen, and chloride or other ions, that react with aluminum to produce a corrosion product with resultant weakening of the aluminum or aluminum alloy structure. To prevent or minimize corrosion, the metal structure is usually provided with a protective coating that is usually applied in one or more layers. In the case of multi-layer coatings, the first or primer layer, that is tenaciously adherent to the metal, typically includes an organic polymer within which is dispersed chromate corrosion-inhibiting compounds. Other layer(s) are then applied over the primer layer. These layer(s) may also be polymer-based and may include colored pigments to produce decorative effects, such as the airline colors. In certain instances, a unilayer coating ("unicoat") is applied which contains the corrosion inhibiting compound and any optional coloring pigments.

25 Recently hexavalent chromate ions have been the subject of health concerns. As a result of these concerns, the United States Environmental Protection Agency (EPA) has promulgated regulations to phase out the use of chromate-type corrosion inhibitors. As a result, alternatives must be found.

30 There exists a need for a chromate-free corrosion inhibitor coating mixture that may be coated over substrates of aluminum and its alloys to protect the substrate from corrosion. More specifically, for the aircraft industry, the corrosion inhibitors must meet high performance criteria. The corrosion inhibitor must be able to prevent detectable pitting corrosion after an aluminum or aluminum alloy substrate, coated with a composition that includes the corrosion inhibitor, has been exposed to a salt spray for 3,000 hours. Moreover, the corrosion inhibitor should not pose the health and environmental hazards that currently raise concerns about chromate inhibitors.

Summary of the Invention

35 The invention provides chromate-free, corrosion-inhibiting coating mixtures, and coatings formed from the coating mixtures. When coated onto a metal substrate, such as an aluminum or aluminum alloy substrate, the coatings are able to withstand a 3,000 hour salt spray test without detectable pitting corrosion on the underlying metal substrate. Moreover, the corrosion-inhibiting compounds do not pose the health hazards associated with hexavalent chromates. In addition, coatings of the invention have a "site blocking" or "buffering" action in that the inhibitors of the coatings are to some extent mobile and can migrate into damaged areas of the coating to protect the damaged area from corrosion. This mobility is a result of the solubility of the corrosion inhibitors in the polymer matrix of the coating.

45 The invention provides corrosion-inhibiting mixtures that includes a film-forming organic polymer, or sol-gel, containing a mixture of chromate-free salts. The mixture of salts includes (1) a first salt selected from (a) the esters of rare earth metals, such as cerium and lanthanum oxalates and acetates, and (b) the vanadate salts of alkali or alkali earth metals, such as sodium metavanadate and calcium metavanadate; and (2) a second salt that is a borate salt of alkali earth metals, such as barium metaborate. It is found that either esters (a) or vanadate salts (b) may be used in conjunction with the borate salts to produce a suitable mixture.

50 A particularly preferred coating contains effective amounts of barium metaborate and sodium metavanadate. In another embodiment, the non-chromate salt is a rare earth chloride, or mixture of rare earth chlorides, or combination of such chlorides with the first salt above, or the second salt above, or both the first and second salts. Examples include cerium chlorid , lanthanum chloride, mixtures of these, and combinations of either with c rium oxalate.

55 The coating mixtures of th invention may b applied to any aluminum or aluminum alloy substrate to provide a protective coating, ither as a primer coat, or as a pigmented coat, or as a unicoat. Typically, the coating is applied to a thickness of from about 0.3 to about 3.0 thousandths of an inch (mils) or at least about 0.01 mils, in the case of sol- g ls. When appli d as a primer or unicoat, the coating of the invention is tenacious, adhering tightly to the underlying aluminum or aluminum alloy substrate. The coatings also meet aviation specifications for withstanding solvent attack and r sistanc to impact. Th coatings are durabl , providing protection even after being subjected to a 3,000 hour

salt spray test. To prevent deterioration of the coatings through exposure to ultraviolet light, the coating may incorporate ultraviolet blockers, pigments for color, and wetting agents may also be added. Moreover, the coating is able to withstand an impact of 50 inch-pounds (forward) and 30 inch-pounds (reverse) as delivered by a Gardner 160 pound capacity impact testing system, without cracking or spalling from the underlying substrate. The coating is also resistant to degradation by solvents, such as SKYDROL, a standard hydraulic fluid used in the civil aviation industry, and its military equivalent.

Detailed Description of the Preferred Embodiments

The invention provides chromate-free coating mixtures and coatings formed from these mixtures that protect an underlying substrate from corrosion. More particularly, preferred embodiments of the invention prevent corrosion of aluminum and its alloys. In general, the coating mixtures include a continuous phase, selected from organic polymers or sol-gels, and a distributed phase, dispersed or dissolved throughout the continuous phase. The distributed phase includes chromate-free salts. In this patent application, the term "chromate-free salts" is used to describe the corrosion inhibiting compounds of the coating mixture or coats formed from the mixture. The term "pigment" is more generally used to apply to other solid additives that may be added to the coatings.

The organic polymers useful in accordance with the invention, include both water-soluble polymers, and those that are soluble in non-aqueous solvents. The useful polymers are those that are film-forming and that crosslink upon drying, either through natural drying or through exposure to ultraviolet light, or through other known means, to produce a cross-linked coating that is substantially insoluble in water. The preferred polymers include for example, epoxies, including polyimide-based epoxies, polyurethanes, acrylic polymers and alkyd-based systems.

Regardless of whether water or solvent-soluble, the preferred polymers are those that meet aviation specifications for withstanding solvent attack, and resistance to impact. Resistance to solvent attack is measured by a standard SKYDROL resistance test, and resistance to impact is measured by the standard Gardner impact test, discussed above. Briefly, the SKYDROL test includes first immersing a coated panel in SKYDROL fluid (or its military equivalent when the coating is for a military aircraft) for 30 days. The panel is then wiped dry and inspected for blistering, loss of coating adhesion or other deterioration. A pencil hardness test is conducted to measure the hardness of the coating. In this test, a squared-off nib of an "HB" hardness pencil is held at a 45° angle to the panel and is pushed along the coating for at least 1/4 inch with sufficient applied force to cause a scratch or crumble the lead nib. If the nib crumbles without scratching the coating, harder pencil numbers are used sequentially until a scratch is visible. The hardness number of this pencil is the "pencil hardness number" of the coating. The SKYDROL resistance of a coating is largely dependent on the SKYDROL resistance of the carrier for the corrosion inhibitors and pigments.

As an alternative, and in a preferred embodiment, a sol-gel, or mixtures of sol-gels, is used instead of, or in addition to, an organic polymer. These sol-gels are known in the art, and are described for example in U.S. Patent Nos. 5,175,027; 5,206,285 and 4,965,091. Sol-gels provide an advantage over polymers in that coatings formed from sol-gel-based coating mixtures are thinner and longer-lasting due to better ultraviolet light resistance, hardness, thermal stability and resistance to oxidation. Moreover, sol-gels may be customized, by selection and functionalization, so that they are compatible with, and adherent to, undercoats (if any), metal (such as aluminum and its alloys), and topcoats (if any). The sol-gels include a variety of inorganic polymeric compounds, including silica-based compounds, such as the silanes of U.S. Patent 5,206,285; and the metal-alkoxide-based sol-gels of U.S. Patents 5,175,027, and 4,965,091.

In accordance with the invention, mixtures of polymers, and mixtures of sol-gels and polymers, may also be used as a carrier for the non-chromate inhibitors, as long as the mixture is able to meet the criteria set forth above. Chromate-free salts, that in combination act as corrosion inhibitors, are distributed throughout this carrier or "continuous phase." Preferably, the mixture of salts has well-controlled solubility in the continuous phase in order to facilitate sustained migration of the inhibitors when a coating formed from the mixture is scratched or otherwise damaged. This mobility is important because it allows the corrosion inhibitors to continue to function to protect an underlying metal substrate by migrating to the exposed metal and protecting the metal from corrosion.

In accordance with the invention, the chromate-free salts are selected from two components: a first component that includes (a) esters of rare earth metals, or (b) vanadate salts of alkali and alkali earth metals; and a second component that includes a borate salt of an alkali earth metal. In certain embodiments, it is preferred that the mixture of salts includes both an ester of a rare earth metal, and a vanadate salt of alkali or alkali earth metals. Thus, in these latter embodiments, the mixture of chromate-free salts includes all three components. Importantly, in all embodiments, the second component should be present in conjunction with at least one first component salt in the coating mixtures of the invention.

Non-limiting examples of the chromate-free salts are: (1) the esters of the first component include cerium and lanthanum oxalates and acetates; (2) the vanadate salts of the first component include sodium metavanadate and calcium metavanadate; and (3) the borate salts of the second component include barium metaborate and calcium borate. Clearly, other salts falling within the generic formulae are also suitable for use in the invention.

In another embodiment, the non-chromate salt is a chloride of the rare earth metals, such as cerium or lanthanum chloride, or mixture of such chlorides. Moreover, the non-chromate salt mixture includes, in addition to the chloride, at least one salt selected from the first and second components, discussed above, or salts selected from both of the components. Thus, for instance, cerium chloride can be mixed with a rare earth ester such as cerium oxalate, or a vanadate such as sodium metavanadate, or both; or a borate such as barium metaborate, or all three of these.

The amount of chromate-free salt required depends upon the severity of the conditions to which the produced coating will be subjected. Therefore, the coating compositions of the invention contain a sufficient amount of chromate-free salt to provide corrosion protection. It is preferred that the coating contain at least about 50 ppm of chromate-free salt, based on the mass of the continuous phase, either organic polymer or sol-gel. Due to cost factors, and diminishing gains in corrosion protection capability, addition of more than about 500 ppm of chromate-free salt is not preferred. However, higher additions may be necessary under conditions that present a severely corrosive environment. Preferably, however, the chromate-free salts are present in an amount ranging from about 50 to about 500 ppm, most preferably about 100 to about 300 ppm.

The coating mixtures of the invention are preferably prepared in liquid form. Thus, the organic polymer is dispersed or dissolved in an appropriate solvent, water or a non-aqueous solvent depending upon the nature of the polymer, and the appropriate amount of chromate-free salt is added. Preferably, the salt is in a fine granular form to facilitate distribution in the polymer blend. As pointed out above, it is preferred that the polymer be selected such that the salts in the polymer have well-controlled solubility. If a polymer, or polymer blend, is selected wherein the salts are not soluble, then the viscosity of the blend should be maintained at a level sufficient to suspend the granular salts throughout the coating mixture. Alternatively, the mixture may be mildly agitated to maintain the salts in suspension as the coating mixture is being applied to a surface.

Likewise, when a sol-gel is used as a continuous phase carrier for the coating mixtures, it is preferred that the chromate-free salts and sol-gels be selected such that the salts are soluble in the sol-gel. Sol-gels have a relatively high viscosity and are not fluid under zero-shear conditions so that once the salts are thoroughly mixed into the sol-gel, the likelihood of the salts settling out is minimal. The sol-gel/salt mixture is then preferably sprayed onto the surface to form a chromate-free coating.

The coating mixtures of the invention may be applied to the surfaces of a metal substrate using any conventional technique, such as spraying, painting with a brush, painting with rollers, dipping, and the like. However, it is preferred that the metal surface be prepared to receive the coating. This preparation includes the conventional method of first cleaning the surface to remove grease and other contaminants. Once the surface is free of surface contaminants, it may be treated to remove any oxide coating, and in certain instances to provide a conversion coating to which the corrosion-inhibiting mixture may more readily bond.

In the event that the surface has a thick oxide coating, then this coating may be removed by conventional means, such as immersion in a series of sequential chemical baths containing concentrated acids and alkalis that remove such a surface coating.

If the surface to be coated is not heavily contaminated with an oxide coating, then it may be treated to provide a conversion coating by immersion in concentrated chromic acid. This process, known in the art and conventional, produces a controlled mixture of aluminum oxides in the surface of an aluminum, or aluminum alloy, substrate. Alternatively, the surface may be treated with a boric acid/sulfuric acid anodizing process. This process, also known in the art and conventional, produces a controlled mixture of aluminum oxides in the surface of an aluminum or aluminum alloy substrate.

Optionally, after the surface has been treated to provide a conversion coating, the surface may be sealed by dipping the substrate into a dilute solution of chromic acid. The clean surface, whether sealed or unsealed, may then be coated with the coating mixtures of the invention.

The following examples illustrate the invention, and do not limit the scope of the invention as described above and as claimed herebelow.

EXAMPLES

Tests were carried out to determine the comparative corrosion protection offered by eleven chromate-free corrosion inhibitor systems on four types of panels that had each undergone a different pretreatment protocol. Tests were also conducted to determine dry adhesion and wet adhesion.

Tests were conducted on sets of aluminum panels, each of which sets had been treated by one of four treatment protocols: the panels were deoxidized through immersion in successive chemical baths only; the panels were treated with concentrated chromic acid to produce a conversion coating of mixed aluminum oxides in the surface; the panels were treated with a boric-sulfuric acid anodize process; or the panels were treated with boric-sulfuric acid anodize process, and then sealed by immersion in dilute chromic acid. The aluminum alloy panels were each of type 2024-T3.

In each case, coating mixtures were prepared using a proprietary polymer, supplied by Deft Chemical Coatings of

17451 Bon Karman Avenue, Irvin , California. The salts in inhibitor mixtures E, F, and G (supplied by D ft Chemical Coatings) contain "molywhite," "halox" and "sicorin RZ." While the actual formulae of these compounds are not known, it is known that they are chromate-free. These coatings contain a borate salt but do not also contain an ester of a rare earth metal, or a vanadate of an alkali or alkali earth metal.

The chromate -free salt mixtures used are shown in Table 1, below:

TABLE 1

<u>Coating Mixture</u>	<u>Salts in Inhibitor Mixture</u>
A	calcium borate + sodium metavanadate
B	sodium metavanadate + cerium acetate + cerium oxalate
C	control using chromate salts (Deft 44-GN series)
D	sodium metavanadate
E	calcium borate + molywhite 101 + zinc phosphate + sicorin RZ
F	calcium borate + molywhite X92 + zinc phosphate + sicorin RZ
G	cerium borate + halox SPZ 391 + zinc phosphate + sicorin RZ
H	cerium acetate
I	cerium oxalate
J	calcium borate
K	cerium acetate
L	cerium oxalate solvent system (Deft 02-GN-58, with catalyst 02-GN-58, and thinner IS-101)

After each pretreated panel in each set of panels had been treated with one of the compositions, A-L (the control is a chromate coating labeled coating C, and the coatings of the invention are A, B, and K), the coatings were allowed to dry. Thereafter, the adhesion strength of each coating to the underlying panel was measured, according to a rating scale from 1-10, with 10 being the most tenacious. Adhesion was also measured after each panel had been exposed to water sprays for seven days. Also the degree of blistering, according to ASTM D 714-87, was measured. This included recording blister sizes, if any, according to a size rating from #1 upward, with #1 being largest. The quantity of blisters produced was also noted as "slight," "medium," or "dense."

To measure corrosion resistance, each panel was inscribed with an "X" after the surface had been pretreated and coated. The "X" was scribed into the panel's surface to a sufficient depth to penetrate any surface coating and to expose underlying metal. Then, each panel was subjected to two corrosion tests: a first test in which a 5 wt.% sodium chloride solution was sprayed onto the coated surface of the panel for 1,500 hours, and a second extended test wherein the spraying was continued for 3,000 hours. Once again, the appearance of the panel was analyzed and recorded. The

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results of both tests are shown in Table 2, Table 3, Table 4, and Table 5 for each of the four sets of pre-treated panels.

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Table 2.

Deoxidized Panels											
SALT MIXTURE	ADHESION		1500 HOURS SALT SPRAY				3000 HOURS SALT SPRAY				OVERALL RATING IN CORROSION
	DRY	7 DAYS WET	STAIN IN SCRIBE	OXIDES IN SCRIBE	BLISTERS	STAIN IN SCRIBE	OXIDES IN SCRIBE	BLISTERS			
A	10	7, #6 MED.	SLIGHT	3	NONE	SOME	3	#4,FEW			FAIR
B	10	9	MEDIUM	2	NONE	MEDIUM	1	#4, FEW			MARGINAL
C	10	3, #8 DENSE	V. SLIGHT	6	NONE	SLIGHT	5	NONE			EXCELLENT
D	10	6, #8 MED.	SLIGHT	4	#4, FEW	SOME	3	#2, FEW			FAIR
E	10	1, #6 MED.	MEDIUM	3	#6, FEW	MEDIUM	2	#4, DENSE			POOR
F	10	1, #6 MED	MEDIUM	3	#4, MED.	MEDIUM	2	#4, DENSE			POOR
G	10	1, #2 DENSE	MEDIUM	4	#4, MED.	MEDIUM	3	#4, DENSE			POOR
H	10	5, MUD CRACK	HEAVY	1	#4, FEW	HEAVY	1	#4, FEW, MUD CRACK			POOR
I	10	7	HEAVY	2	NONE	HEAVY	1	NONE			MARGINAL
J	10	1, #8 MED.	HEAVY	2	#6, MED.	HEAVY	2	#6, DENSE			POOR
K	10	10	HEAVY	1	#2, FEW	HEAVY	1	#2, FEW			POOR
L	10	6, #6 MED.	MEDIUM	2	NONE	HEAVY	1	#4, FEW			MARGINAL

Table 3.

Conversion Coated Panels										
SALT MIXTURE	ADHESION		1500 HOURS SALT SPRAY			3000 HOURS SALT SPRAY			OVERALL RATING IN CORROSION	
	DRY	7 DAYS WET	STAIN IN SCRIBE	OXIDES IN SCRIBE	BLISTERS	STAIN IN SCRIBE	OXIDES IN SCRIBE	BLISTERS		
A	10	10	SOME	4	NONE	MEDIUM	3	NONE	GOOD	
B	10	10	MEDIUM	3	NONE	HEAVY	2	NONE	MARGINAL	
C	10	10	V. SLIGHT	6	NONE	SLIGHT	5	NONE	EXCELLENT	
D	10	10	SOME	4	NONE	MEDIUM	3	NONE	GOOD	
E	10	10	MEDIUM	3	NONE	HEAVY	2	NONE	FAIR	
F	10	9	HEAVY	2	NONE	HEAVY	2	NONE	FAIR	
G	10	10	MEDIUM	3	NONE	HEAVY	2	NONE	FAIR	
H	10	10	HEAVY	1	NONE	HEAVY	0	NONE	POOR	
I	10	10	HEAVY	1	NONE	HEAVY	0	NONE	POOR	
J	10	10, #8 FEW	HEAVY	2	NONE	HEAVY	1	#8, DENSE	POOR	
K	10	10	HEAVY	1	NONE	HEAVY	0	NONE	MARGINAL	
L	10	10	SLIGHT	5	NONE	SOME	4	NONE	GOOD	

Table 4,
Boric-Sulfuric Acid Treated Panels

SALT MIXTURE	ADHESION		1500 HOURS SALT SPRAY				3000 HOURS SALT SPRAY				OVERALL RATING IN CORROSION
	DRY	7 DAYS WET	STAIN IN SCRIBE	OXIDES IN SCRIBE	BLISTERS	STAIN IN SCRIBE	OXIDES IN SCRIBE	BLISTERS	STAIN IN SCRIBE	OXIDES IN SCRIBE	
A	10	10	SLIGHT	5	NONE	SOME	4	NONE	SOME	4	EXCELLENT
B	10	9	SOME	4	NONE	MEDIUM	3	NONE	MEDIUM	3	GOOD
C	10	10	V. SLIGHT	5	NONE	SLIGHT	5	NONE	SLIGHT	5	EXCELLENT
D	10	7	V. SLIGHT	5	NONE	SLIGHT	4-5	NONE	SLIGHT	4-5	EXCELLENT
E	10	1, #4 MED.	MEDIUM	3	NONE	MEDIUM	3	#8, MED.	MEDIUM	3	POOR
F	10	1, #4 DENSE	MEDIUM	3	#8, FEW	HEAVY	2	#8, DENSE	HEAVY	2	POOR
G	10	4, #4, FEW	SOME	3-4	NONE	MEDIUM	2-3	NONE	MEDIUM	2-3	FAIR
H	10	8	HEAVY	1	NONE	HEAVY	1	NONE	HEAVY	1	POOR
I	10	10	HEAVY	1	NONE	HEAVY	0	NONE	HEAVY	0	POOR
J	10	1, #6, MED.	MEDIUM	2-3	NONE	HEAVY	1	#8, DENSE	HEAVY	1	POOR
K	10	7, #8, MED.	HEAVY	1	NONE	HEAVY	0	NONE	HEAVY	0	POOR
L	10	8	SOME	3	NONE	MEDIUM	3	NONE	MEDIUM	3	GOOD

Table 5,

Boric-Sulfuric Acid Treated and Sealed Panels											
SALT MIXTURE	ADHESION		1500 HOURS SALT SPRAY				3000 HOURS SALT SPRAY				OVERALL RATING IN CORROSION
	DRY	7 DAYS WET	STAIN IN SCRIBE	OXIDES IN SCRIBE	BLISTERS	STAIN IN SCRIBE	OXIDES IN SCRIBE	BLISTERS			
A	10	10	SOME	3	NONE	MEDIUM	3	NONE	FAIR		
B	10	8	MEDIUM	3	NONE	HEAVY	2	NONE	FAIR		
C	10	10, #8, FEW	V. SLIGHT	6	NONE	SLIGHT	5	NONE	EXCELLENT		
D	10	7, #8, MED.	SLIGHT	5	NONE	SOME	4-5	NONE	EXCELLENT		
E	10	1, #2, DENSE	SOME	3	#8, FEW	MEDIUM	3	#8, DENSE	MARGINAL		
F	10	1, #4, DENSE	SOME	3-4	NONE	MEDIUM	3	#8, DENSE	MARGINAL		
G	10	1, #6, MED.	SLIGHT	4-5	NONE	SOME	4	#8, DENSE	GOOD		
H	10	7, #8, MED.	HEAVY	1	NONE	HEAVY	0	NONE	POOR		
I	10	10	HEAVY	2	NONE	HEAVY	1	NONE	POOR		
J	10	1, #6, MED.	MEDIUM	3	#8, FEW	HEAVY	3	#8, DENSE	MARGINAL		
K	10	2, #8, MED.	HEAVY	3-4	NONE	HEAVY	3	NONE	FAIR		
L	10	10	SLIGHT	5	NONE	SOME	4-5	NONE	EXCELLENT		

Th panels treated by deoxidation only, Table 2, do not fairly represent the type of surface treatments typically used in the aircraft industry. However, all the coatings passed the dry adhesion test, while only coatings A, B, I and K passed the wet adhesion test. Coating A, according to the invention, exhibited excellent performance in the 3,000 hour corrosion test, with fair performance in the scribed areas. Thus, coating A compared well with the control, C, using a chromate-based coating.

All mixtures coated onto panels with a conversion coating, Table 3, passed the dry adhesion test. Also, all except J had excellent wet adhesion. Once again, coating A showed good performance, compared to the "excellent" performance of the control, in the 3,000 hour corrosion test. Only coatings D and L had comparable performance.

The coated boric-sulfuric acid anodized panels, Table 4, showed excellent dry adhesion for all coatings, and only coatings E, F and G failed the adhesion test. A coating according to the invention, coating A, had excellent adhesion performance, and excellent salt spray corrosion resistance. Only the control and comparative coating D showed comparable results. This shows that the coating of the invention is comparable to chromate-inhibitor systems and is useful as a substitute for the chromate systems.

The coated boric-sulfuric acid anodized and sealed panels each showed excellent adhesion performance, and the invention coating A and the Control C showed excellent wet adhesion performance. However, while the control showed excellent corrosion resistance after 3,000 hours, the system of the invention, A, showed fair performance.

The results of the tests are encouraging, indicating that the coating compositions of the invention provide performance characteristics rivaling those of the control chromate-based coatings.

While the preferred embodiment of the invention has been illustrated and described, it will be appreciated that various changes can be made therein without departing from the spirit and scope of the invention.

Claims

1. A corrosion-inhibiting coating mixture, the mixture comprising:

- (a) a film-forming organic polymeric component; and
- (b) a sufficient quantity of a chromate-free mixture of salts distributed in the polymeric component to, upon drying, produce a coating that, when coated onto aluminum or an alloy thereof, withstands a 3,000 hour salt spray without significant corrosion of the aluminum or aluminum alloys, the mixture comprising:

- (i) a salt selected from the group consisting of an ester of a rare earth metal, and a vanadate salt of an alkali or alkali earth metal; and
- (ii) a borate salt of an alkali earth metal.

2. The coating mixture of claim 1, wherein the film-forming organic polymer is selected from the group consisting of: epoxy-based polymers, polyimides, polyurethanes, acrylics and alkyd-based polymer systems.

3. The coating mixture of claim 1 or 2, further comprising a chloride salt of a rare earth metal.

4. The coating mixture of claim 1, 2 or 3, wherein the mixture of salts comprising at least about 50 ppm of a salt selected from the group consisting of an ester of a rare earth metal and a vanadate of an alkali or alkali earth metal.

5. A corrosion-inhibiting coating mixture, the mixture comprising:

- (a) a sol-gel component; and
- (b) a sufficient quantity of a chromate-free mixture of salts distributed in the polymeric component to, upon drying, produce a coating that, when coated onto aluminum or an alloy thereof, withstands a 3,000 hour salt spray without significant corrosion of the aluminum or aluminum alloys, the mixture comprising:

- (i) a salt selected from the group consisting of an ester of a rare earth metal, and a vanadate salt of an alkali or alkali earth metal; and
- (ii) a borate salt of an alkali earth metal.

6. The coating mixture of claim 5, wherein a dried coating formed from the mixture has the property of mobility of at least one of the mixture of salts in the coating.

7. The coating mixture of claim 5 or 6, further comprising an organic polymer compatible with the sol-gel.

8. The coating mixture of claim 5, 6 or 7, further comprising a chloride salt of a rare earth metal.
9. The coating mixture of any of claims 1-8, wherein the chromate-free mixture of salts comprises about 50 to about 500 ppm of the chloride salt.
10. The coating mixture of any of claims 1-9, wherein the chromate-free mixture of salts comprises about 100 to 300 ppm of the mixture.
11. The coating mixture of any of claims 1-10, wherein the mixture of salts comprises from about 100 to about 300 ppm of the coating.
12. A coating on a metallic skin of an aircraft, the coating comprising:
 - (a) a continuous phase of a composition selected from the group consisting of organic polymers and sol-gels; and
 - (b) a mixture of chromate-free salts dispersed throughout the matrix, the mixture comprising:
 - (i) a salt selected from the group consisting of an ester of a rare earth metal, and a vanadate salt of an alkali or alkali earth metal; and
 - (ii) a borate salt of an alkali earth metal;wherein the coating protects the metallic coating from significant pitting corrosion after 3,000 hours of exposure to a spray of 5 wt. % sodium chloride solution; wherein the coating is resistant to degradation by SKYDROL; and wherein the coating is able to withstand a 50-inch-pound forward impact delivered by a Gardner 160 pound capacity test machine.
13. The coating of any of claims 1-12, wherein the mixture of salts comprises from about 50 to about 500 ppm of the ester.
14. The coating of any of the claims 1-13, wherein the mixture of salts comprises from about 50 to about 500 ppm vanadate salt.
15. The coating of any of the claims 1-14, wherein the mixture of salts comprises from about 50 to about 500 ppm borate salt.
16. The coating of any of the claims 12-15, wherein the salts are mobile in the coating and able to migrate areas of the coating to protect exposed underlying substrate.
17. A corrosion-inhibiting coating mixture, the mixture comprising:
 - (a) a film-forming polymeric component; and
 - (b) a sufficient quantity of a chromate-free chloride of a rare earth metal distributed in the filmforming component to, upon drying, produce a coating that, when coated onto aluminum or an alloy thereof, is able to withstand a 3,000 hour salt spray without significant corrosion of the aluminum or aluminum alloys.
18. The coating mixture of claim 17, wherein the film-forming component is selected from the sol-gels and organic polymers.
19. The coating mixture of claim 17 or 18, wherein the chromate-free salt selected from lanthanum chloride and cerium chloride.
20. The coating mixture of claim 18, 19 or 20, wherein the chromate-free salt comprises:
 - (a) a salt selected from the group consisting of an ester of a rare earth metal, and a vanadate salt of an alkali or alkali earth metal; and
 - (b) a borate salt of an alkali earth metal.



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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 5 064 468 A (TOSHIHIRO OKAI) * abstract * * column 2, line 35-38 * * column 3, line 4-9 * * column 3, line 17-26 * * column 4, line 33-35 * * column 4, line 45-58 * * column 5, line 20-22 * ---	1,2,4	C09D5/08
A	US 4 064 028 A (YOSHIKI MIYOSAWA) * abstract * * column 4, line 50 - column 5, line 8 * ---	1	
A	US 4 049 596 A (ANDREW TRAISTER) * claims * ---	1	
A	US 5 077 332 A (PAUL BLATTNER) * claims * ---	1	
X	EP 0 696 624 A (NIPPON PAINT CO) * abstract * * page 2, line 41-42 * ---	17,19	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	US 5 221 371 A (ROBERT N. MILLER) -----	17,19	C09D C23F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 2 June 1997	Examiner Girard, Y
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons @ : member of the same patent family, corresponding document</p>			